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Modelling the response of soil and soil solution chemistry upon roofing a forest in an area with high nitrogen deposition

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Abstract

In the Speuld forest, the Netherlands, the dynamic soil acidification model NuCSAM has been applied to a manipulation experiment in which part of the forest was roofed to control nitrogen (N) and sulphur (S) deposition. The roofed area was divided into two subplots watered artificially; one received ambient N and S deposition and one with pristine N and S deposition. Concentration measurements on each plots showed a high (time-dependent) spatial variability. Statistical analyses of the concentrations on both subplots showed small but significant effects of the reduction in deposition on nitrate (NO_3), sulphate (SO_4) and aluminium (Al) concentrations. The statistical significance of the effects was minimised by the large spatial variability within the plots. Despite these shortcomings, simulated concentrations were generally within the 95% confidence interval of the measurements although the effect of a reduction in N deposition on soil solution chemistry was underestimated due to a marked decline in N-uptake by the vegetation.

Introduction

Soil chemical conditions in forest ecosystems in the Netherlands are affected strongly by high sulphur dioxide (SO_2), nitrogen oxide (NO_x) and reduced hydrogen (NH_y) deposition levels. Even though the deposition of S has decreased substantially over the last decade (Erisman and Bleeker, 1997), levels of NO_x and NH_y are still high and have caused high N content in the foliage and forest floor and high concentrations of ammonium (NH_4), NO_3, hydrogen (H^+) and Al in the soil solution. This, which in turn, may lead to a reduction in biodiversity and tree vitality and an increase in groundwater pollution (De Vries *et al.*, 1995).

The present policy is to reduce deposition levels in the Netherlands to critical levels by the year 2010. Several soil chemical models such as MAGIC (Cosby *et al.*, 1985), SMART (De Vries *et al.*, 1989), SAFE (Warfvinge *et al.*, 1993) and NuCSAM (Groenenberg *et al.*, 1995) have been developed to simulate the effects of changes in deposition on the chemical composition of the soil solid phase and soil solution. Several of these models have simulated successfully changes in the soil solution and the soil solid phase over the past decade (Kros and Warfvinge, 1995), when changes in deposition levels of N were, relatively small. Consequently, model performance in the case of a sudden marked reduction in N deposition could not be tested using these datasets.

Within the framework of the NITREX (Nitrogen Saturation Experiments) programme, manipulation studies were carried out at eight forest stands across Europe (Wright and Van Breemen, 1995). At the Dutch manipulation sites, Speuld and Ysselsteyn, deposition of N and S was reduced to pre-industrial levels by roofing a part of the stand. Results from these experiments can be used to test the ability of soil chemical models to predict the soil chemical conditions which will be observed following a marked reduction in deposition rates.

In model validation studies, model predictions are often compared with observations made at a single point in space or with averages. Field soils, however, show a strong spatial variability as shown for example by Tiktak *et al.* (1988) for the Speuld experimental forest, where variations in soil texture occur over very short distances. Small overall differences in soil solution chemistry may be obscured by this strong spatial variability. Moreover, as travel times of solutes from point to point also differ in response to variable throughfall amounts (Bouten *et al.*, 1992), the determination of an average soil solution composition is unreliable and an alternative is to calculate the 95% confidence intervals of the observations. The model is

accepted if the model predictions fall within this range, thus taking into account that validation of the model is limited by the uncertainty in the observations (Parrish and Smith, 1990).

In this paper, the NuCSAM model is applied to the experimental site at Speuld to study whether the model would yield acceptable predictions of the changes in solute concentrations in response to a marked reduction in deposition. Firstly, the model was parameterized for a control plot with ambient deposition, after which the model was validated using data from the roofed plot with reduced deposition.

Material and methods

RESEARCH SITE

The research site is near the village of Speuld in the Veluwe area of the central Netherlands (52°13′N, 5°39′E) at an altitude of 50 m. Measurements at this 2.5 ha site were started in 1986 by the Dutch Priority Program on Acidification (DPPA); part of this site was reserved for N manipulation experiments in 1989.

The area around Speuld is a rolling forest and heathland. The forests are of Douglas fir (Pseudotsuga menziesii (Mirb.) Franco), Scots pine (*Pinus sylvestris* L.), oak (*Quercus robur* L.) and beech (*Fagus sylvatica* L.), and are surrounded by agricultural land. The climate is temperate and humid, with a mean annual temperature of approximately 10°C and a mean annual precipitation of approximately 800 mm.

The research site is forested almost exclusively with Douglas fir (provenance Arlington) planted in 1962 as two-year old seedlings. The soil was neither ploughed nor fertilized. The stand was thinned in 1969 and 1976 but further thinning, although needed, has been postponed lest it affects the ongoing research. Consequently, the stand is so dense (800–1200 stems ha^{-1}) that little light reaches the forest floor, and no ground vegetation layer has developed. The trees are 18–20 m high and are in vitality class 2; this indicates a needle loss of 10–25%. No needle discoloration was observed. Deciduous forests of about the same height surround the site.

The soil is a well drained Typic Dystrochrept (USDA) or Cambic podzol (FAO) developed in heterogeneous ice-pushed river sediments with a sandy loam to loamy sand texture (Tiktak *et al.*, 1988). Throughout each year the water table was at a depth greater than 40 m.

ROOF EXPERIMENT

In 1989, the NITREX research site was established to perform N input manipulations. Ambient throughfall water was intercepted by a transparent roof and replaced by demineralised (clean) water to which all nutrients were added in the same amount as present in the ambient throughfall except for N and S. Below the roof (14 m × 28 m), two plots (10 m × 10 m) were set up to receive either clean water (roof-clean) or ambient throughfall (roof-control). The roof was built below the canopy and was 2–3 m in height. Throughfall water caught on the roof was either stored (ambient plot) or replaced by clean rainwater (clean plot). Until 1992, the water collected was sprayed in weekly doses. In February 1992 the watering regime was changed to an almost real time watering. By means of sensors in the storage containers, the watering was adjusted such that spraying followed each 2 mm of precipitation.

MONITORING

Input fluxes, pressure heads and soil solution concentrations were monitored between 1989 and 1994. Every fortnight bulk precipitation was collected in a sampler (diameter 24.6 cm) in a clearing near the site, while throughfall precipitation was collected in five samplers (diameter 9.6 cm) per plot. Stemflow was not collected.

Pressure heads were measured daily by means of 4 tensiometers located in the roof-control plots at a depth of 90 cm. An additional tensiometer was located at 250 cm depth. Soil moisture contents were not measured.

In each plot, soil water was collected at five depths (0, 10, 25, 45 and 90 cm from the surface of the mineral soil) using 8 replicates for the 10 cm depth and 4 replicates for the remaining depths. Soil water was collected every two weeks using ceramic cups to which a vacuum (–70 kPa) was applied. At 0 cm, ceramic plates with a siphon system and a 5 litre storage bottle were used (*cf.* Boxman *et al.*, 1995). Soil water could not be collected during dry periods.

Nutrient contents were measured yearly in young needles (0.5 year) and older needles (>1.5 year). Litterfall and nutrient contents in litterfall were measured 4 to 6 times a year from the litter collected on the roof.

EVALUATION OF THE DATASET

Soil solution composition and soil moisture conditions in the Speuld forest tend to show strong variation in space. This variation was mainly caused by local differences in litterfall and throughfall amounts and composition, by associated differences in the magnitude of biochemical processes like root uptake and mineralization and by differences in soil texture and soil chemical properties. To determine the limitations of the dataset, the extent of the variation in observed soil solution composition and soil moisture content and the significance of the observed effects of reducing the deposition were evaluated.

To evaluate model performance, both the magnitude of the observations of soil solution concentrations and pressure heads and the pattern of the changes with time are important. The uncertainty in the magnitude of the obser-

vations is quantified by calculating the average and the standard error of the observations at each timestep. The changes with time in the average observations may show a distorted picture when the observations do not have a uniform pattern. For example, when the succession of peaks and dips in the concentration measurements of the different cups is out of phase, the average pattern will be damped compared to the pattern of the original cups. To compare the pattern of the average concentrations with the simulation results it is necessary to prove that the measured concentration patterns of the different cups are similar.

The similarity of the patterns was investigated by statistical analyses of the datasets. When a uniform pattern does exist, the concentrations in one cup are approximately a constant multiple of the concentration in another cup, i.e. the differences of the log of the concentrations of the two cups are constant. In this case the log of the concentrations as a function of time can be fitted as a function of cup and the individual points in time, representing the dips and peaks in the concentration measurements:

$$\log C_{i,t} = D_i + \log C_{r,t} \quad (1)$$

where $C_{i,t}$ is the concentration measured with cup i at time t, D_i is the difference between cup i and a reference cup and $C_{r,t}$ is the concentration measured with the reference cup. The reference cup, at each depth, was chosen arbitrarily from the 4 to 8 cups. When the concentration measurements do not show a uniform pattern, the above model can be improved significantly by taking into account the interaction between time and cup (i.e. D_i has a different value at each time) indicating that the behaviour of the individual cups is time dependent. The interaction between time and cup is described by a spline function, using a number of parameters which is equal to a quarter of sampling dates.

The reduction of deposition of S and N in the 'pristine' (pre-industrial) roofed plot is expected to reduce SO_4, NO_3 and Al concentrations and increase pH compared to the plot with ambient deposition. The observations were fitted by a multiple-linear regression model as a function of the plot (clean or ambient), the individual measurement points of time and the interaction term between plot and time. When a significant decrease in concentrations has occurred in the pristine plot the interaction term between plot and time will lead to a significant improvement of the model.

MODEL DESCRIPTION

NuCSAM is an integrated soil acidification model that simulates the major hydrological and biogeochemical processes in the forest canopy, litter layer and mineral soil. (Groenenberg *et al.*, 1995; Tiktak *et al.*, 1995). Processes included are: evapotranspiration, canopy interception, water transport, canopy interactions, litterfall, root decay, mineralization, nitrification, denitrification, root uptake, cation exchange, SO_4 sorption, weathering of minerals and Al, protonation of organic anions and the dissociation of inorganic carbon (C) and solute transport. An overview of the process formulations is given in the Appendix.

Hydrology is modelled with an adapted version of SWATRE (Belmans *et al.*, 1983; Groenenberg *et al.*, 1995). The change in soil solution chemistry is calculated from a set of mass balance equations describing the input, output and interactions in each compartment. Vertical heterogeneity is taken into account by differentiating between soil layers. The soil layers are considered as homogenous compartments of constant density and the constituent input mixes completely within each soil layer.

In NuCSAM, both exogenous and endogenous organic matter are distinguished (Groenenberg *et al.*, 1999). Organic matter is divided over three pools with their own transformation and mineralization rates (Appendix; Eqn. 3).

Uptake of nutrients is described by a demand function, which consists of maintenance uptake and growth uptake (Appendix; Eqn. 4). Growth is modelled with a logistic growth curve. The uptake demand for growth is calculated by multiplying the growth with the preset fixed contents of the different biomass compartments. The N content in needles is variable and depends on the optimal N content which is a linear function of total N deposition and the amount of N which can be provided by root uptake. The maintenance uptake demand is calculated from the balance of litterfall, foliar exudation, foliar uptake and rootdeath.

The weathering of silicates is described by a first order rate equation, the dissolution of amorphous Al compounds is calculated by an Elovich equation and ion-exchange is described by the Gaines-Thomas equation (see Appendix; Eqn. 11).

For its application to the roof experiment, NuCSAM was adapted slightly. Normally throughfall, canopy interactions and the optimal N content in the needles are calculated by NuCSAM from the wet and dry deposition on the canopy. Upon roofing, the forest natural throughfall is replaced by a sprinkling solution. Because the roof was established below the canopy, canopy interactions remain unchanged. Accordingly, in the adapted version of NuCSAM, throughfall composition was set equal to the composition of the sprinkling water, whereas the calculation of the canopy interactions remains unaltered. The optimal N content in leaves, which is normally calculated from the N deposition on the canopy is now calculated from the amounts added by sprinkling.

MODEL EVALUATION

NuCSAM was calibrated on the roofed site with ambient deposition. Next, the calibrated model was applied to the roofed site with pristine deposition. Calibration was performed by comparing the observations with the associated

model results, taking into account the precision of the observations. As a criterion for selecting the best model calibration, the model capability index was chosen (see below); this was minimized by trial and error. The hydrological submodel was calibrated on pressure heads (only available at 90 cm depth) and on measured chloride (Cl) concentrations at 10, 25, 45 and 90 cm depth. The soil chemical model was calibrated on measured concentrations in the soil solution. Optimised parameters were the air entry value in the Van Genuchten formula which describes the soil physical characteristics, the SO_4 adsorption capacity and the mineralization rate parameters.

The variation in the measured concentration was considerable. For each solute, at 10, 25, 45 and 90 cm depth, the percentage of model predictions which did not fall within the 95% confidence interval and the model capability index (Parrish and Smith, 1990) was calculated. The model capability index (C) indicates the factor with which the model over- or under-estimates the observations. To obtain a measure for the average model performance during the simulation period, individual values of the model capability index were averaged over the simulation period (Tiktak *et al.*, 1998). The index was calculated as:

$$C_i = \frac{\sum_{t=0}^{nt} \begin{cases} L_{i,t} / P_{i,t} & \text{if} \quad P_{i,t} < L_{i,t} \\ 1 & \text{if} \quad L_{i,t} < P_{i,t} < U_{i,t} \\ P_{i,t} / U_{i,t} & \text{if} \quad P_{i,t} > U_{i,t} \end{cases}}{nt} \tag{2}$$

where $P_{i,t}$ is the model prediction for solute i at time t, $L_{i,t}$ is the lower limit of the 95% confidence interval $U_{i,t}$ is the upper limit of the confidence interval of solute i at time t and nt is the number of points in time at which both observations and simulation results are available. Soil solution concentrations were measured bi-weekly, whenever the water content was high enough for sampling; this occurred on 53 to 76 observation dates for the whole period. $L_{i,t}$ and $U_{i,t}$ are calculated by the following equations, assuming that the observations are normally distributed:

$$L_{i,t} = \overline{x_{i,t}} - t_{(n-1)} \cdot S_{\overline{x},i,t} \tag{3}$$

$$U_{i,t} = \overline{x_{i,t}} + t_{(n-1)} \cdot S_{\overline{x},i,t} \tag{4}$$

where $\bar{x}_{i,t}$ is the average of the observations, t_{n-1} is the appropriate value of the t distribution for $n-1$ observations and $S_{\bar{x}i,t}$ is the standard error of the observed mean for solute i at time t. The number of observations at time t ranged from 2 to 4 in the subsoils and from 2 to 8 in the topsoil. To calculate $L_{i,t}$ and $U_{i,t}$, it was assumed that observations were normally distributed. This assumption was tested for a number of measurements at 10 cm depth and appeared to be justifiable for most elements. However, the NO_3 concentrations in the plot with pristine deposition levels could be described by a normal distribution only after log-transformation of the data.

Another, more commonly used, measure to evaluate the model performance is the root mean square error (RMSE), which is defined as:

$$RMSE_i = \sqrt{\frac{\sum_{t=1}^{nt} (P_{i,t} - O_{i,t})^2}{nt}} \tag{5}$$

in which $P_{i,t}$ is the simulated concentration of solute i at time t and $O_{i,t}$ is the average measured concentrations of solute i at time t. If the model describes the dataset accurately, then RMSE should approximate the standard error in the measurements.

Model input

To compare the model results with the average measurements at both the plot with pristine and ambient deposition model inputs which represent the average situation in these plots must be selected. Unfortunately, all the data needed to run NuCSAM were not available for the roofed sites and thus data from nearby parts of the Speuld forest (unroofed control plot, monitoring plot from the Dutch Priority Programme on Acidification (DPPA), ecophysiological research plot and a clearing close to the forest) had to be used to complete the dataset. Moreover, the same data, except for the atmospheric deposition, were used for both subplots, disregarding spatial variability between the subplots.

DEPOSITION

Total deposition, dry deposition and canopy exchange fluxes were derived from the bi-weekly measurements of bulk precipitation and throughfall. Yearly deposition fluxes (Table 1) and canopy exchange fluxes were calculated using the sodium-filtering approach (Ulrich, 1983; Van der Maas and Pape, 1990; Draaijers, 1993). Canopy exchange parameters, as used in NuCSAM (see Appendix, Eqn. 1), were calculated from these yearly fluxes (Table 2). Bi-weekly total deposition fluxes were derived using these canopy exchange parameters and the measured bi-weekly bulk deposition and throughfall data. Deposition fluxes for the roofed plot were calculated from the amount and the composition of the solution sprinkled under the roof.

HYDROLOGICAL DATA

Daily average temperature and global radiation were measured at the weather station 'De Bilt' (50 km from the site) and daily precipitation data from Putten (10 km from the site). Total amounts of precipitation, measured at Putten, were adjusted using the bi-weekly measured amounts at a clearing close to the site. 30 year average precipitation at Putten is 842 mm a^{-1} and the yearly average temperature is 9.3°C. Precipitations at the Speuld site during the simulation period were 894, 750, 1035, 1033 and 1182 mm in 1990, 1991, 1992, 1993 and 1994, respectively.

Table 1. Average deposition and canopy exchange fluxes over the period 1990—1994 ($mol_c.ha^{-1}.a^{-1}$) for the unroofed situation and for the roofed plots.

	H	NH_4	NO_3	SO_4	K	Ca	Mg	Na	Cl
Unroofed									
WD	220	924	430	683	72	128	144	635	883
DD	–196	1856	424	1200	56	137	113	449	472
TD	24	2781	854	1884	128	265	257	1084	1355
CE	–10	–278	0	0	228	35	26	0	0
Roofed plot with ambient deposition									
WD	5	2122	556	1690	480	367	309	966	1320
DD	0	0	0	0	0	0	0	0	0
TD	5	2122	556	1690	480	367	309	966	1320
CE	–10	–278	0	0	228	35	26	0	0
Roofed plot with reduced deposition									
WD	12	197	156	142	451	428	191	480	1320
DD	0	0	0	0	0	0	0	0	0
TD	12	197	156	142	451	428	191	480	1320
CE	–10	–278	0	0	228	35	26	0	0

WD = Wet deposition
DD = Dry deposition
TD = Total deposition
CE = Canopy exchange

Table 2. Values for soil-layer independent model parameters.

Process	Parameter[a]	Unit	Value
Foliar uptake[b]	$frNH_{4,fu}$	(–)	0.11
	frH_{fu}	(–)	0.43
Foliar exudation b[b]	$frCa_{fe}$	(–)	0.12
	$frMg_{fe}$	(–)	0.09
	frK_{fe}	(–)	0.79
Mineralization[c]	$k_{mi,lt}$	(a^{-1})	0.31
	$k_{mi,fm}$	(a^{-1})	0.008
	$k_{mi,hu}$	(a^{-1})	0.002
	$k_{tr,lt}$	(a^{-1})	0.15
	$k_{tr,fm}$	(a^{-1})	0.01
Nitrification[c]	k_{ni}	(a^{-1})	100.0
Al dissolution[d]	KAl_{ox}	(l^2 mol^{-2})	5.0×10^8

[a] For symbols see Appendix
[b] Based on bulk deposition and throughfall data over the period 1990–1994.
[c] Obtained by calibration.
[d] Average *IAP* for $Al(OH)_3$ at 90 cm over the period 1987–1990, activities calculated from measured concentrations (Van der Maas and Pape, 1990).

Parameters used to calculate throughfall were taken from a previous model application of NuCSAM to the DPPA plot (Tiktak *et al.*, 1995). Root distribution was based on root length distribution measurements in the DPPA plot (Olsthoorn, 1991). Average water retention characteristics and conductivity data for the Speuld forest were available for the upper 50 cm of the profile (Tiktak *et al.*, 1990); for the deeper soil layers, data from the DPPA plot were used (Tiktak and Bouten, 1990).

BIOCHEMICAL DATA

An overview of the necessary biomass data is given in Table 3. Stem biomass data were derived, using regression functions (Dik, 1984), from yearly diameter measurements of the trees in the plots combined with tree height measurements in the ecophysiological research plot, close to the roofed plot (Steingröver and Jans, 1995). These stem biomass data were fitted with a logistic growth curve (see Eqn. 4, Appendix). Nutrient contents in branches, stems

Table 3. Biomass data used as input to NuCSAM.

Parameter	Symbol[a]	Unit	Value
Stand age	age_{lt}	(a)	30
Logistic growth constant	kr_{grl}	(a^{-1})	0.094
Maximum amount of stems per ha	$Amst_{mx}$	(Mg ha^{-1})	543.8
Amount of foliage per ha	Am_{lv}	(Mg ha^{-1})	18.5
Half life time growth function	*t05*	(a^{-1})	38
Branch stem ratio	fr_{brst}	(–)	0.11
Litter fall rate constant	*klf*	(a^{-1})	0.13

[a] For symbols see Appendix

and coarse roots (Table 4) were based on data from Berdowski *et al.* (1991) for the ecophysiological research plot. Nutrient contents in fine roots were taken from measurements at the DPPA plot (Olsthoorn, 1991). Nutrient contents in needles were based on measurements on the plots. Litterfall rate constants were derived by dividing the measured yearly litterfall data by the weight of needles measured in the ecophysiological research plot (Steingröver and Jans, 1995).

Mineralization rates were based on the accumulation of ecto-organic layers on 150 forest stands in the Netherlands (De Vries and Leeters, 1998) by solving the mass balance equations for organic matter analytically (Groenenberg *et al.*, 1999). The average values obtained for Douglas fir were adapted slightly for the Speuld forest on the basis of the mass of organic matter accumulated on the forest floor (Table 2). Nitrification rate (Table 2) parameters were assumed equal to those used for the DPPA application.

GEOCHEMICAL DATA

Most geochemical parameters and rate constants were taken equal to values used for the NuCSAM application to the DPPA plot (Tiktak *et al.*, 1995). Cation exchange capacity (CEC) and adsorbed cations were based on measurements of soil samples from the two plots in 1992 (Table 5). Gaines-Thomas exchange constants were calculated from the measured adsorbed amounts in 1992 and the average soil solution concentrations during 1992. No significant differences existed between the amounts adsorbed in the two roofed plots. Therefore, average values of both plots were used. Sulphate sorption capacity (SSC; $mmol_c\ kg^{-1}$) was calculated from the NH_4-oxalate extractable Al ($ctAl_{ox}$) amount according to Johnson and Todd (1983):

Table 4. Data on biomass and element contents of needles, roots and stems.

Compartment[a]	Biomass (Mg ha^{-1})	Element content (% of dry weight)				
		N	K	Ca	Mg	S
Foliage (Am_{lv})	18.5	1.31	0.18	0.42	0.07	0.15
Branches (Am_{br})[b]	14.0	0.30	0.10	0.05	0.03	0.05
Stems (Am_{st})	60.0	0.20	0.10	0.05	0.01	0.05
Fine roots (Am_{rt})[c]	3.2	1.00	0.08	0.16	0.04	0.10
Litter (Am_{lt})[d]	35.0	—	—	—	—	—

[a] For symbol see Appendix.
[b] Nutrient contents in branches, wood and roots inferred from general data (Berdowski *et al.*, 1991).
[c] Measured in the soil research plot of the DPPA plot by Olsthoorn (1991).
[d] Measured by Tiktak and Bouten (1992). The litter mass is an average value for 485 samples. Element contents in litter are calculated by the model using the foliage contents as initial values.

Table 5. Average adsorbed amount of base cations in 1992 and Gaines-Thomas exchange constants for the roofed plots.

Depth (cm)	Adsorbed amounts ($mmol_c\ kg^{-1}$)				Exchange constants relative to Ca[a] (mol $l^{-1})^{z-2}$					
	Al	BC	NH_4	H	Al	H	NH_4	K	Na	Mg
10	13.6	2.5	0.5	7.9	0.02	3224	1192	1667	1.4	0.4
25	9.4	0.9	0.1	0.9	0.21	2560	4485	2066	1.5	0.4
50	4.0	0.5	0.1	0.4	0.07	4185	35279	3064	18.4	0.5
90	2.9	0.3	0.03	0.1	0.05	4104	11605	369	6.1	0.2

[a] z refers to the charge of the ion involved in the ion-exchange reaction against Ca.

$$SSC = 0.02 \cdot ctAl_{ox} \quad (6)$$

NH_4-oxalate extractable Al, was not measured for the NITREX plots and thus data were based on the DPPA dataset.

Results and discussion

OBSERVED SOIL MOISTURE CONDITIONS

Differences in measured pressure heads (Fig. 1) between the four tensiometers were limited in the (wet) winter periods (coefficient of variation <3%); however, strong variations were found during dry periods (coefficient of variation up to 42%). Tensiometers 1 and 2 showed the fastest and strongest increase in measured pF values during dry periods; the other tensiometers reacted more slowly. The response of tensiometer 3 was very irregular. In 1991, the pattern of measured pF values of tensiometer 3 was comparable to tensiometer 4. In 1992 and 1993, its reaction was comparable to tensiometer 2 and, in 1994, pF values measured by this tensiometer were nearly constant.

OBSERVED SOIL SOLUTION CHEMISTRY

Marked fluctuations in soil solution concentrations were found between the individual cups in both the roofed plots with ambient and with pristine deposition. The average concentrations with standard errors during the measurement period is given in Table 6. The coefficient of variation ranged between 30 and 150%. Accordingly, the 95% confidence interval around the measurements was rather broad (Fig. 2a, b and c for the roofed plot with ambient deposition), especially in dry periods when no soil solution could be extracted. Moreover, the lack of soil solution data from the cups in the dryer part of the plot may lead to an underestimation of the average concentrations during these dry periods.

The pattern of dips and peaks in concentration measurements of the individual cups with time was analyzed by regression analysis, to evaluate whether the simulated pattern could be compared with the measured pattern. When a uniform pattern was assumed, the fitted model could account for 25 to 60% (average 45.6%) of the variance in the concentrations. The model which assumed a non-uniform pattern performed much better (on average this model accounted for 83.3% of the variance). The results were confirmed by a visual comparison of the Cl concentration measurements at 10 and 90 cm depth for the plot with ambient deposition (Fig. 1). At 10 cm depth, only three out of the eight measured cups are shown. Sometimes (e.g. April 1992, at 10 and 90 cm depth), the timing of dips and peaks coincided for all cups; at other times, a clear shift in the peaks of the individual cups was found (e.g. autumn 1993 and spring 1994 (10 cm)). Moreover, some cups showed a gradual shift in concentration over the measurement period with respect to the other cups. For example, at 90 cm depth, the Cl concentrations measured with cup 35 were one of the highest in 1991 and nearly the lowest at the end of the measurement period in 1994. The pattern of the average concentrations (Fig. 3) is damped compared to the original measurements, due to the observed differences in patterns between the individual cups.

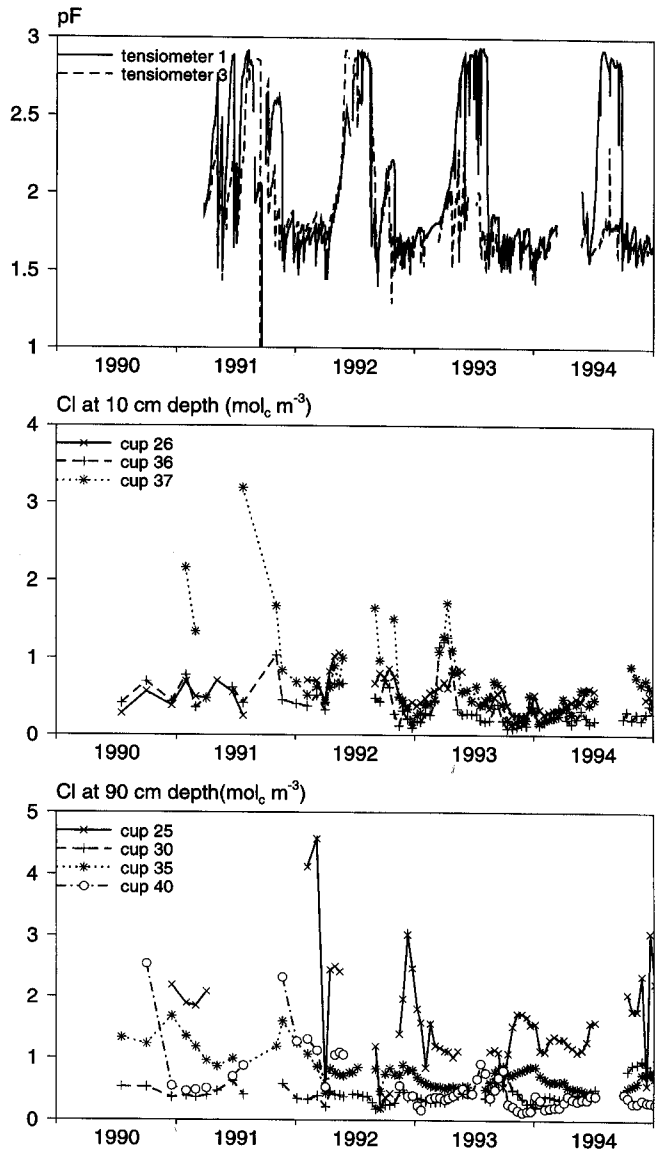

Fig. 1. *Measured pressure heads at 90 cm depth and measured Cl concentrations at 10 and 90 cm depth at the roofed plot with ambient deposition.*

Concentrations of SO_4 and NO_3 were significantly higher and pH values were significantly lower in the plot with ambient deposition levels compared to the plot with pristine deposition levels (Fig. 4a, b and c, Table 6). Statistical analysis showed very significant differences in the concentrations of SO_4, NO_3, Al and pH between the

Fig. 2a

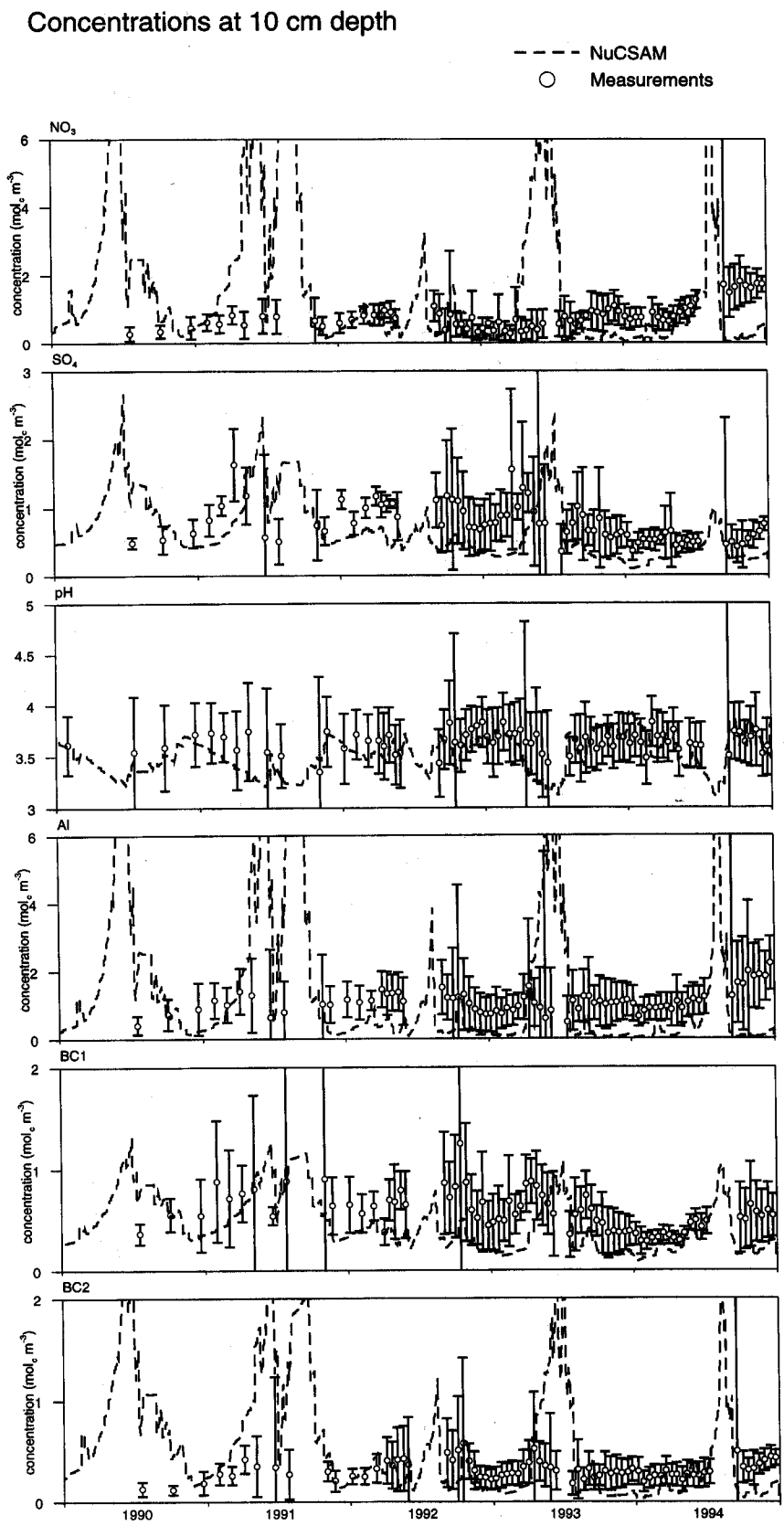

Fig. 2. *Measured and simulated concentrations of NO_3, SO_4, Al, BC1 (K+Na) and BC2 (Ca+Mg) and pH at 10, 45 and 90 cm depth at the roofed plot with ambient deposition. Error bars indicate the 95% confidence interval of the measurements.*

Fig. 2b

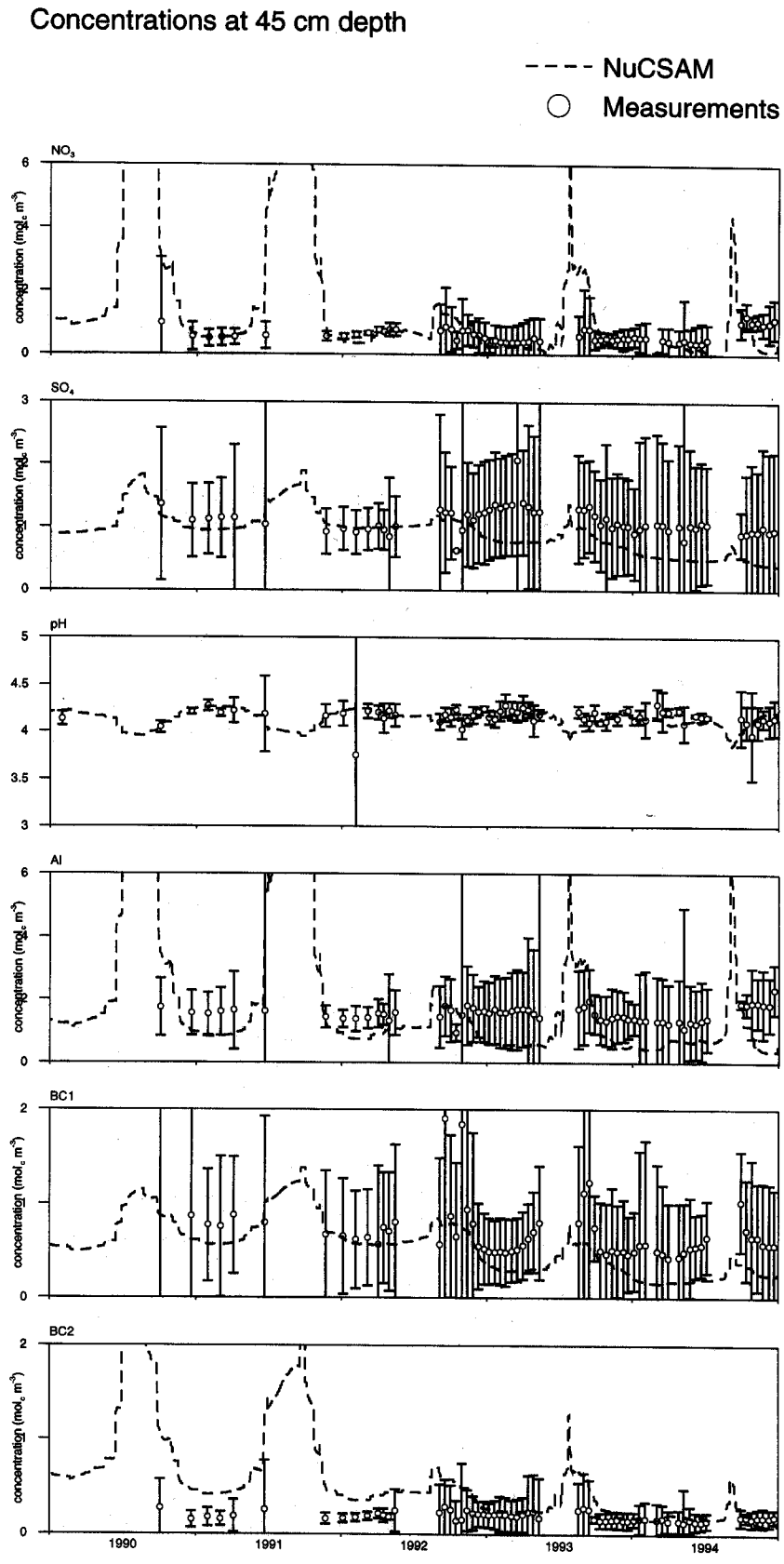
Concentrations at 45 cm depth
NuCSAM
Measurements
NO3
SO4
pH
Al
BC1
BC2
concentration (molc m-3)
1990
1991
1992
1993
1994

Fig. 2c

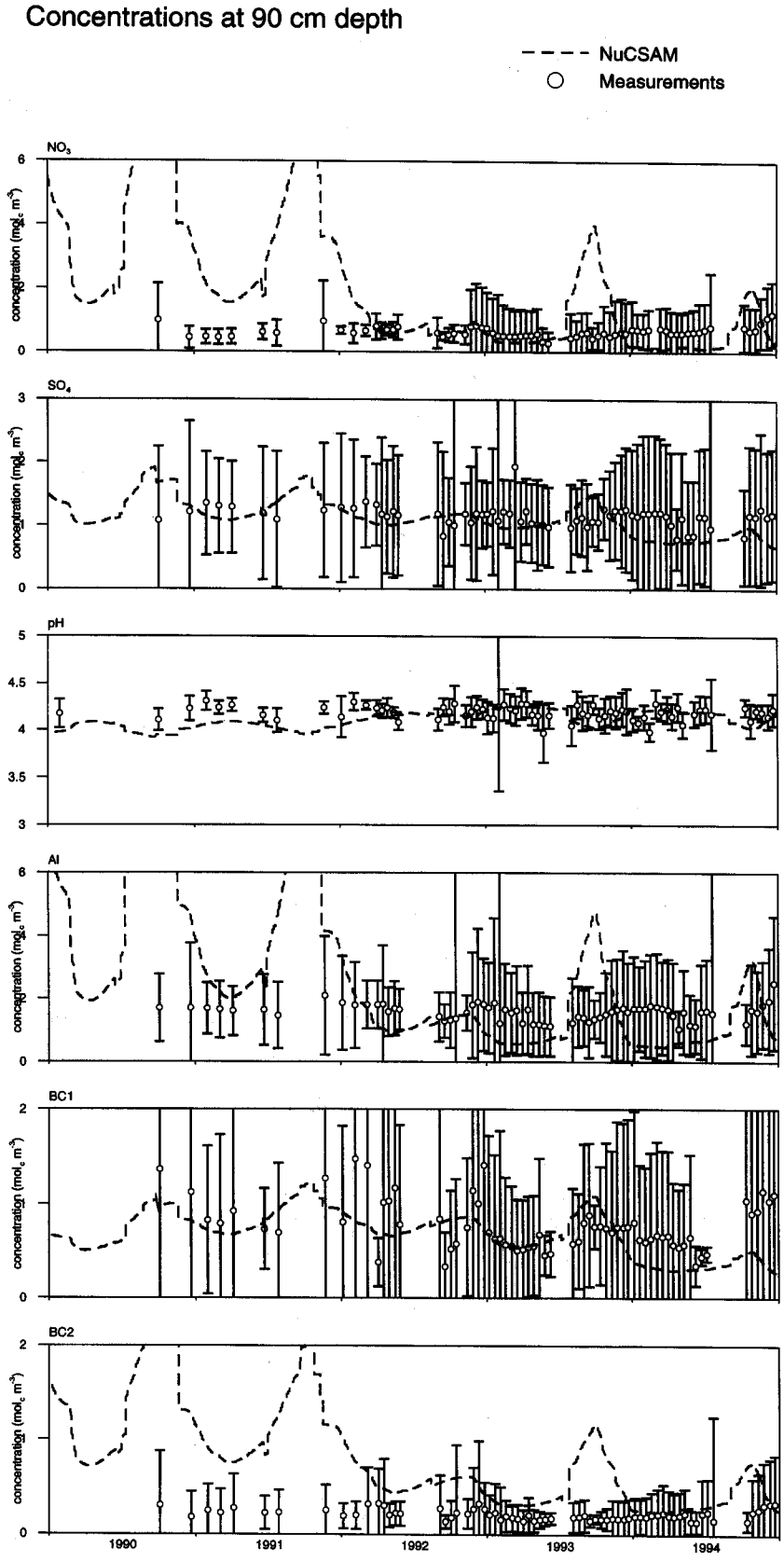
Concentrations at 90 cm depth
NuCSAM
Measurements
NO3
SO4
pH
Al
BC1
BC2
concentration (molc m-3)
1990
1991
1992
1993
1994

Table 6. Average measured soil solution concentrations (c) and standard error (se) ($mol_c\ m^{-3}$) at 10, 45 and 90 cm depth during the monitoring period (1989–1994) for the roofed plots with ambient and clean deposition.

Solute	Ambient deposition						Clean deposition					
	10 cm		45 cm		90 cm		10 cm		45 cm		90 cm	
	c	se	c	se	c	se	c	se	c	se	c	se
pH	3.6	0.3	4.2	0.1	4.2	0.1	3.8	0.2	4.2	0.1	4.2	0.1
Al	0.37	0.21	0.51	0.17	0.52	0.22	0.27	0.19	0.34	0.13	0.45	0.16
Ca	0.07	0.03	0.03	0.01	0.04	0.02	0.05	0.04	0.02	0.01	0.03	0.02
Mg	0.09	0.04	0.06	0.02	0.07	0.05	0.06	0.04	0.05	0.04	0.04	0.04
K	0.03	0.03	0.01	0.01	0.03	0.02	0.02	0.03	0.02	0.02	0.03	0.02
NH_4	0.04	0.04	0.01	0.01	0.01	0.01	0.02	0.02	0.00	0.00	0.01	0.01
NO_3	0.80	0.38	0.61	0.25	0.64	0.36	0.33	0.44	0.14	0.23	0.21	0.33
SO_4	0.38	0.14	0.54	0.23	0.57	0.24	0.17	0.12	0.33	0.09	0.47	0.14
Cl	0.55	0.25	0.73	0.40	0.78	0.54	0.68	0.37	1.00	0.76	1.07	0.77

two plots. The effect of the reduction in deposition was relatively small but a significant effect was found in the NO_3 concentrations at 10, 25, 45 and 90 cm. A significant decrease of the SO_4 concentration with time was found at 45 and 90 cm depth, whereas no significant effects were found at 10 and 25 cm. For Al, a significant effect was found at 10, 45 and 90 cm and, for pH, significant effects were found only at the 25 and 90 cm depths.

That only slightly significant effects of reductions in deposition were found is due partly to the considerable spatial variability within the plots, coupled with the absence of concentration measurements at the start of the experiment (up to July 1990). This is a major limitation as results of a comparable roof-experiment in Solling, Germany, showed that the largest changes in soil solution chemistry occurred during the first month of the experiment (Bredemeier *et al.*, 1995). Furthermore, the effect of roofing the plots might overshadow the influence of deposition reduction through: (i) changes in frequency, spatial distribution and amount of rainfall, (ii) unintended reduction of (NO_3) deposition on the ambient roofed plot during 1990 and 1991, with respect to the natural situation, resulting from denitrification during storage of the sprinkling solution and (iii) changes in biochemical processes due to small changes in temperature and moisture (Gundersen *et al.*, 1997).

SIMULATED HYDROLOGY

pF values in the winter period were underestimated by the model. The model simulated a pF of circa 2.0 during these periods while measured pF values where approximately 1.6. This problem could be solved by adaptation of the parameter α, the reciprocal of the air entry value, in the Van Genuchten formula (Van Genuchten, 1980). To obtain the best correspondence between measured and simulated pF values α was increased from 0.04 to 0.095 m^{-1}. During the simulation period 39% of the simulated pF values where within the 95% confidence interval of the measurements. Simulated values were mostly within the 95% confidence interval during late winter and spring; pF values in autumn (rewetting of the soil) were generally overestimated (Fig. 3). A more thorough calibration of the soil physical characteristics was considered excessive, due to the lack of sufficient information (water contents and pressure heads in the topsoil) to identify the influence of the various parameters on the model results.

The performance of the hydrological submodel was further evaluated by comparing measured and simulated chloride (Cl) concentrations (Fig. 3) because Cl concentrations are governed mainly by the magnitude of the Cl deposition fluxes and the hydrological processes. Most (86.5%) of the simulated Cl concentrations at 90 cm depth fell within the 95% confidence interval of the measured concentrations (Table 7). The average deviation between the measured and the simulated values is low (C-index = 1.05) and the RMSE of the simulations is close to the standard error of the observations (Table 8). Although pressure heads at this depth were generally overestimated in autumn, Cl concentrations during this period were within the 95% confidence interval. However, simulated Cl concentrations were higher than average values during this period whereas they were lower than average in the remaining part of the year. Also the confidence interval of the Cl concentrations measurements (Table 6) was generally wider than that for the measurements of the pressure heads. Comparable results for the simulation of Cl were found at 45 cm depth (Table 7). The performance of the model in the topsoil was less satisfactory. Cl concentrations were frequently underestimated especially in the

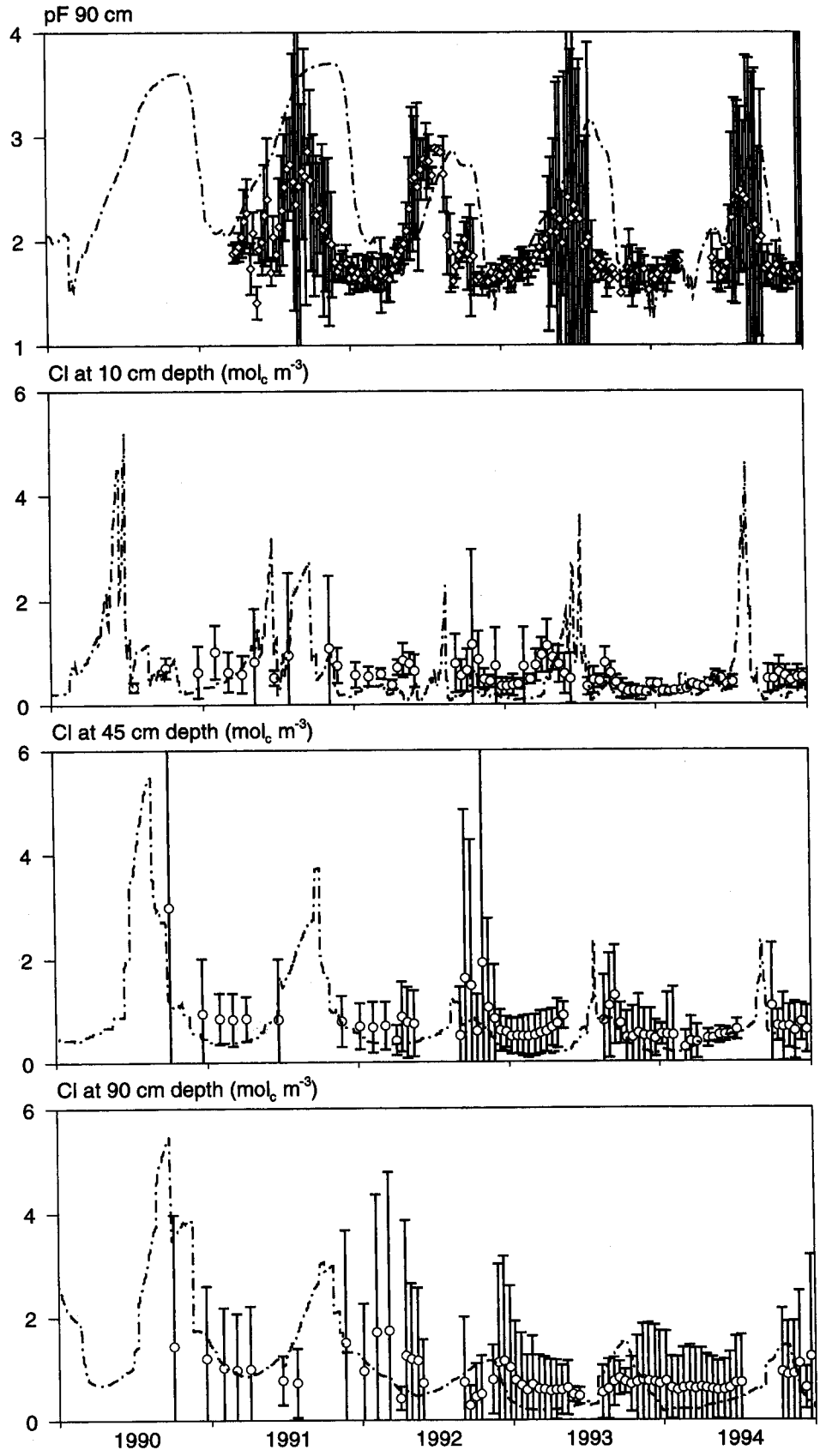

Fig. 3. *Simulated and measured pF at 90 cm depth and Cl concentrations at 10, 45 and 90 cm depth at the roofed plot with ambient deposition. The error bars indicate the boundaries of 95% confidence interval of the measurements.*

Fig. 4*a*

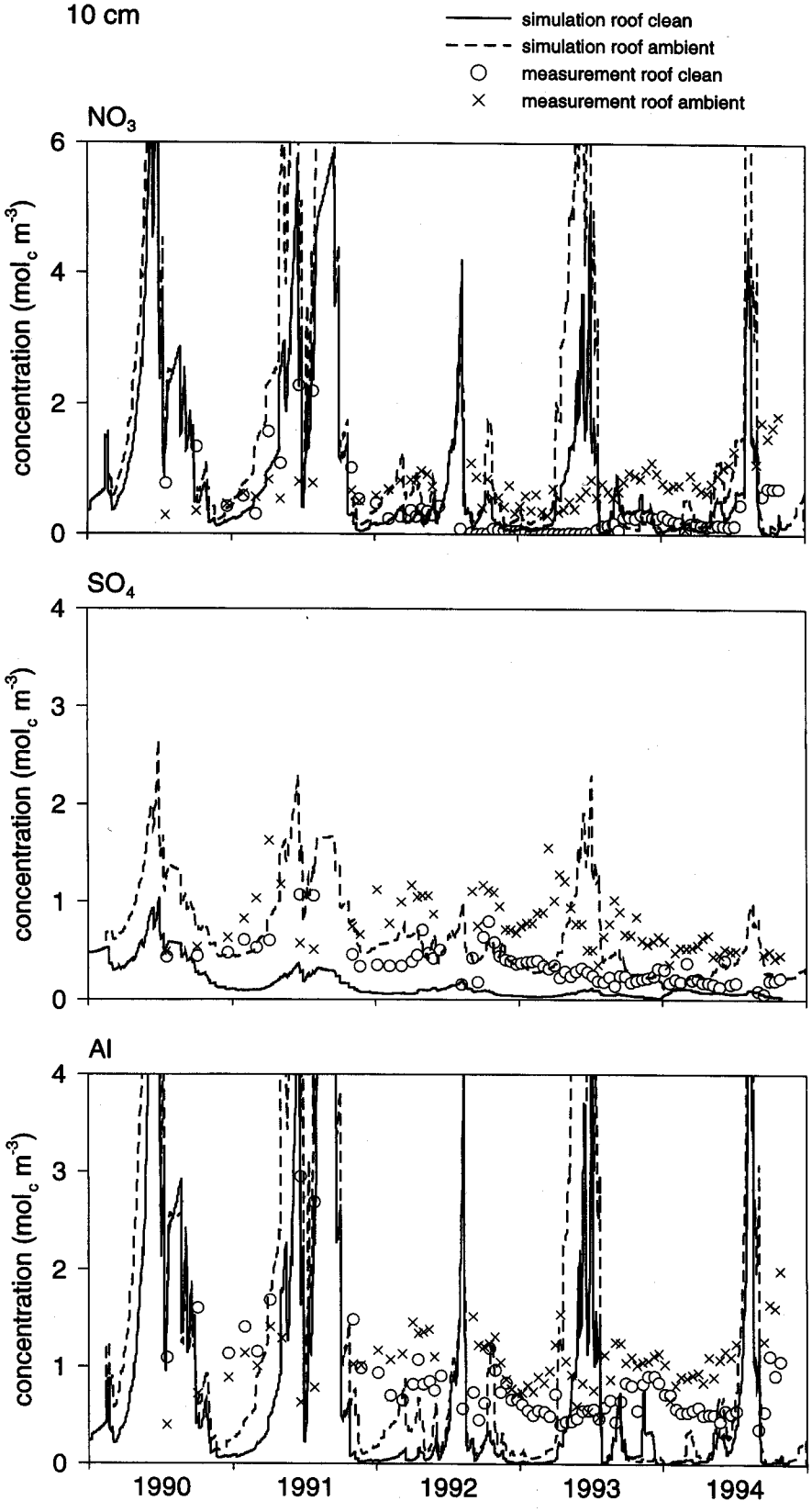

Fig. 4. *Average measured concentrations and simulated concentrations of SO_4, NO_3 and Al for the roofed plot with ambient and clean deposition at 10, 45 and 90 cm depth.*

Fig. 4*b*

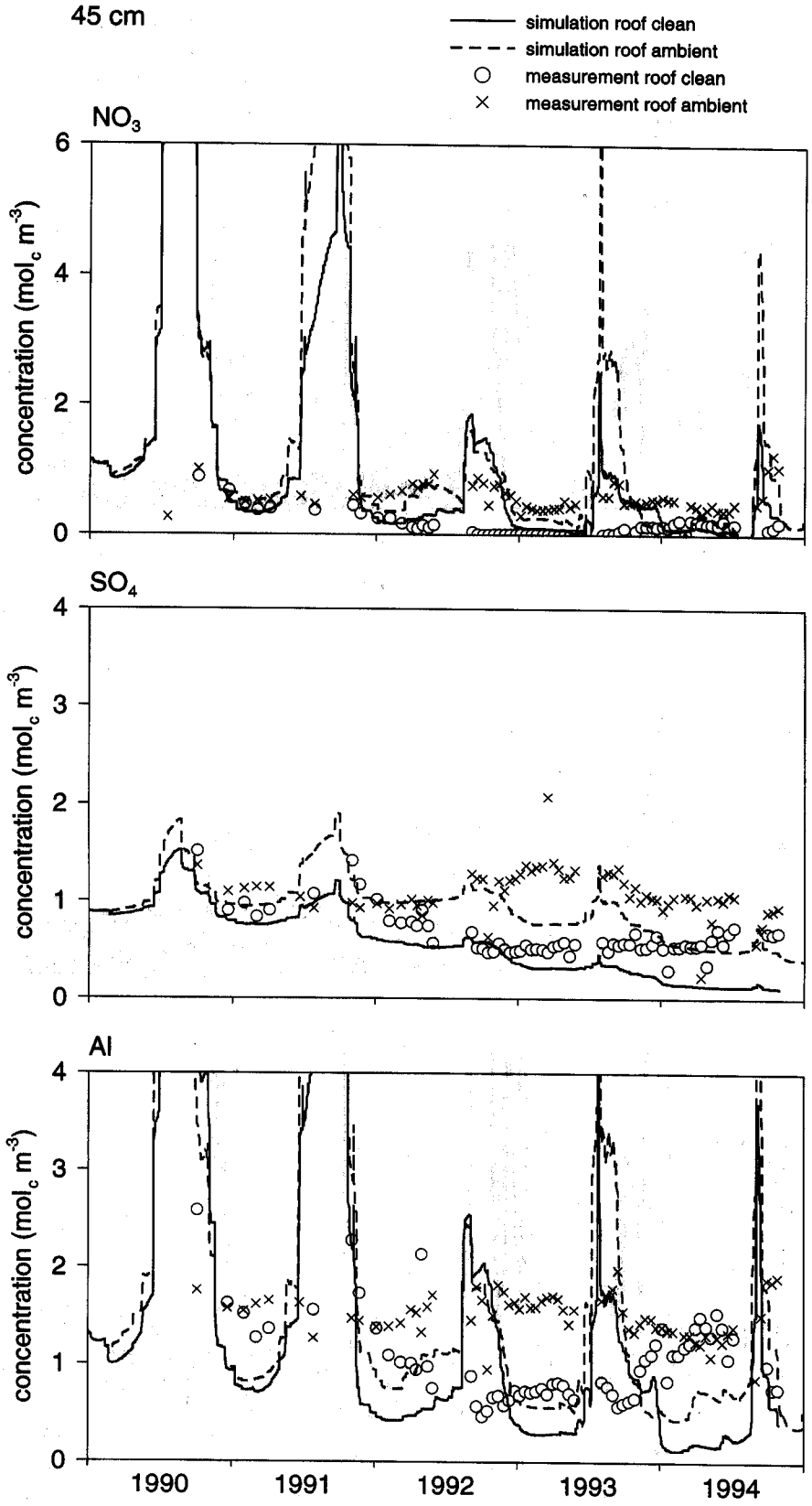
45 cm
simulation roof clean
simulation roof ambient
measurement roof clean
measurement roof ambient
NO3
SO4
Al
concentration (molc m-3)
0
1
2
3
4
6
1990
1991
1992
1993
1994

Fig. 4c

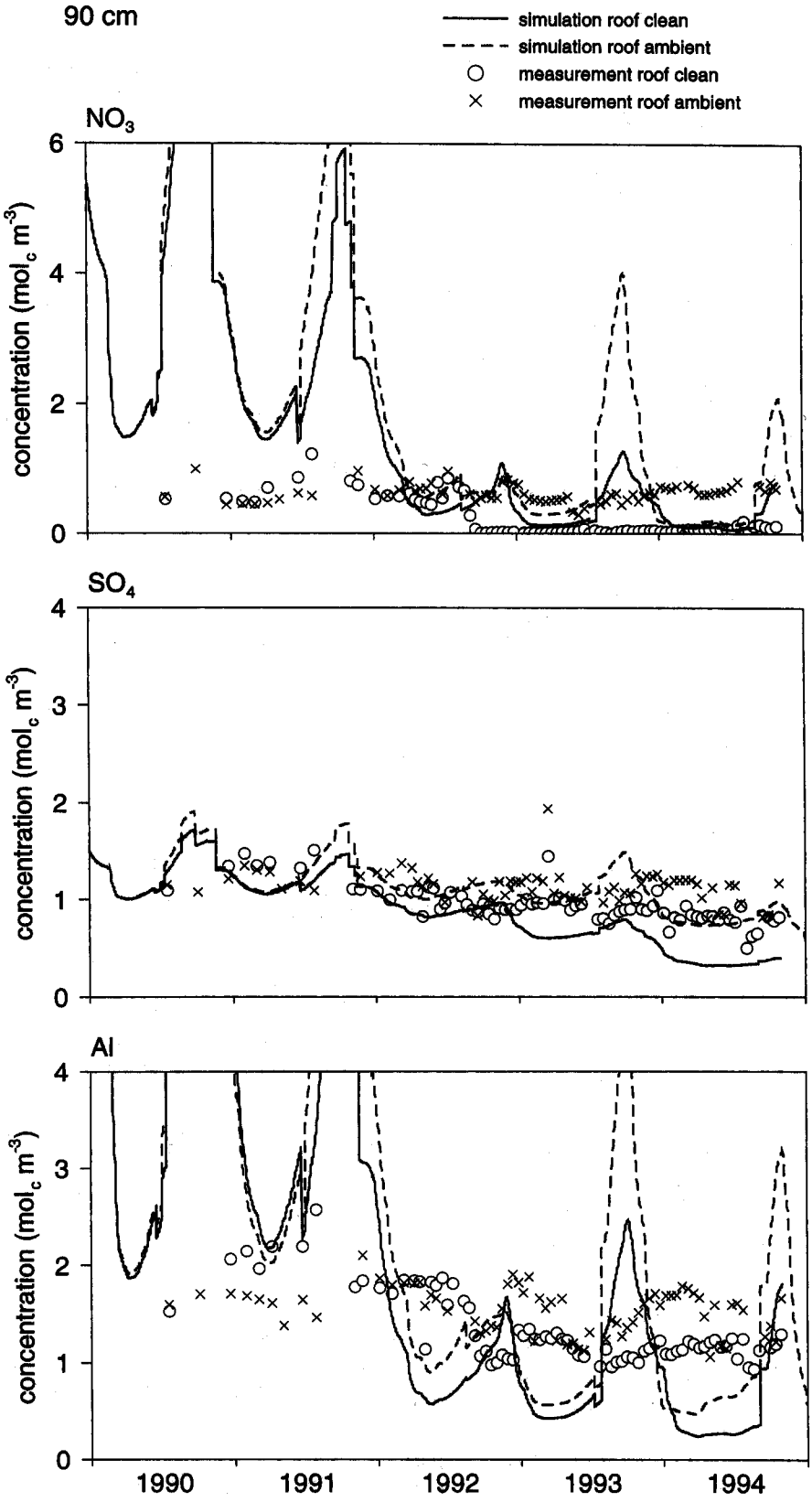
90 cm
simulation roof clean
simulation roof ambient
measurement roof clean
measurement roof ambient
NO3
SO4
Al
concentration (molc m-3)
0
1
2
3
4
6
1990
1991
1992
1993
1994

Table 7. Percentage of the simulation results outside the 95% confidence interval of the measurements (deviation) and the C-index for the plot with ambient and clean deposition.

Solute	Ambient deposition						Clean deposition[1]					
	Deviation (%)			C-index			Deviation (%)			C-index		
	10 cm	45 cm	90 cm	10 cm	45 cm	90 cm	10 cm	45 cm	90 cm	10 cm	45 cm	90 cm
pH	10.7	21.1	25.0	1.00	1.00	1.01	28.0	13.8	35.1	1.01	1.00	1.00
Al	77.6	32.9	21.3	4.84	1.18	1.12	45.9	25.0	43.4	7.97	1.17	1.34
BC1[2]	57.3	5.8	6.8	1.27	1.01	1.01	34.2	6.2	0.0	1.31	1.01	1.00
BC2[2]	56.6	40.0	49.3	1.72	1.22	1.54	35.1	40.6	57.9	1.46	1.20	1.45
NH_4	83.1	85.9	17.1	4.83	4.47	1.10	88.2	95.4	35.4	6.19	10.18	1.24
NO_3	66.2	33.8	35.5	3.70	1.48	1.46	34.7	15.1	26.9	9.76	4.18	1.58
SO_4	59.2	1.4	1.3	1.39	1.01	1.00	37.8	25.0	23.7	1.95	1.13	1.08
Cl	72.0	14.5	13.5	1.58	1.15	1.05	53.4	9.4	5.4	1.71	1.02	1.03

[1] Fig.s for NO_3 concentrations at the plot with clean deposition are based on log-transformed data.
[2] BC1= (K+Na); BC2 = Ca + Mg.

winter period. The average deviation between measured and simulated values was within a factor of two of the measurements (C-index = 1.6 and 1.75 and RMSE = 0.41 and 0.65 for the ambient and clean plot, respectively). The observed discrepancies between measurements and simulation results may well be caused by the use of suboptimal data for soil physical characteristics. However, spatial differences between the plot averaged throughfall amounts and composition (as used in the model) and throughfall at the points where the cups and tensiometers are placed may also contribute to the discrepancies. This aspect is probably more important than in a natural situation, because the sprinklers lead to a higher spatial variability in water distribution compared to natural throughfall (Gundersen *et al.*, 1997).

On the plot with clean deposition, Cl concentrations at 45 and 90 cm depth were slightly better simulated (lower C-index and lower percentage of simulation outside the 85% confidence interval) which at 10 cm depth, the C index was somewhat higher compared to the calibration site, although, the percentage of simulations outside the 95% interval was nearly 19% lower.

Table 8. Root mean square error for the simulation of the concentrations on the plot with ambient and clean deposition.

Solute	Ambient deposition			Clean depostion		
	10 cm	45 cm	90 cm	10 cm	45 cm	90 cm
pH	0.18	0.10	0.12	0.25	0.13	0.11
Al	1.71	1.42	2.10	0.60	0.95	1.29
BC1[2]	0.32	0.48	0.28	0.26	0.48	0.42
BC2[2]	0.47	0.38	0.59	0.27	0.25	0.42
NH_4	0.15	0.04	0.01	0.12	0.05	0.01
NO_3	1.81	1.60	1.54	0.72	0.71	0.92
SO_4	0.40	0.38	0.53	0.13	0.18	0.32
Cl	0.41	0.65	0.55	0.53	0.81	0.66

[2] BC1= (K+Na); BC2=Ca+Mg.

SIMULATED SOIL SOLUTION CHEMISTRY

Plot with ambient deposition

An overview of the measured and simulated concentrations of the main solutes at 10, 45 and 90 cm depth is given in Figs. 2a, b and c. The results were obtained almost without calibration of the process parameters describing the bio-geochemical interactions. Only the SO_4 sulphate adsorption capacity was decreased by a factor 3 compared to the DPPA dataset. The lower values for the SSC may be due to a lower amount of NH_4-oxalate extractable Al at the roofed plots compared to the DPPA plot or to differences between the actual SSC at Speuld and the SSC predicted by the pedo-transfer function (Eqn. 5).

The slight underestimation of the measured Cl concentrations by NuCSAM at 10 cm depth was also found for the other concentrations at this depth. More than 50% of the time the simulated concentrations did not fall within the 95% confidence interval of the measurements. The average deviation from the confidence interval was, however, relatively small as indicated by the C-index and the RMSE (Table 7), except for NO_3, Al and NH_4. pH values were well simulated by the model; most values were within the 95% confidence interval, the C-index was 1.002 and the RMSE was smaller or equal to the standard error of the observations. The discrepancies between the measurements and the simulation results of NO_3 and Al were clearly higher than for the other elements because of the high concentrations simulated in spring and summer. The model performance for NH_4 was also poor. However, both measured and modelled concentrations are extremely low

(<0.04 mol_c m^{-3}) and the observed discrepancies are not very important to the overall performance of the model.

The results at 45 and 90 cm depth generally corresponded better with the measurements than those in the topsoil, which coincides with the better hydrological simulation results (see Cl concentrations). Just as in the topsoil, NO_3 and Al concentrations were overestimated during the summer period, especially at 90 cm depth during 1990 and 1991. NUCSAM also overestimated divalent base cations during this period, probably due to the exchange of Ca against Al on the adsorption complex.

The high simulated NO_3 concentrations may be caused by an underestimation of the NO_3 uptake and/or denitrification and an overestimation of the (net) mineralization rate. During the first two years of the experiment N deposition below the roof was reduced by 50% compared to the ambient deposition on the unroofed plot. This was due to the loss of N by denitrification during storage of the throughfall used for sprinkling. This reduction in N deposition led to an underestimation of the N content in the needles (1.6%) compared to the measured N content (1.8%). Apparently, the relationship between the optimal N content in the needles and N deposition used in NuCSAM caused a too strong reduction in N uptake. Due to this reduction in N demand by the needles, simulated N uptake was reduced to 25% of the average value. Similar problems were encountered with the application of the model MAGIC to a deposition reduction experiment in Solling, Germany (Alewell *et al.*, 1997). Model parameters in MAGIC, relating the N uptake with the NO_3 deposition had to be increased by a factor 4 to simulate measured concentrations in Solling.

To quantify the effect of the reduced N uptake on the simulated NO_3 concentrations an additional run with NuCSAM was carried out in which the optimal N content in the needles was related to the (50% higher) deposition on the canopy instead of the deposition beneath the roof. With this adapted version of NuCSAM, simulated N content in the needles (1.9%) corresponded with measured N content in the needles. The simulated NO_3 concentrations at 10 and 45 cm depth, however, were only slightly lower than previously. At 90 cm depth the effect was somewhat larger, but NO_3 concentrations were still higher than measured especially during the first two years and during dry periods. These results indicate that an underestimation of the denitrification and/or an overestimation of the mineralization rate is of even more importance to the simulated NO_3 concentrations. In NuCSAM, daily mineralization and (de)nitrification fluxes are calculated from a year average value that is based on C/N ratio of the litterfall and humus layer and the average groundwater table, and a given seasonal distribution of those fluxes. A direct feedback between the mineralization and (de)nitrification fluxes and temperature and soil moisture content is not implemented in the present version of NuCSAM.

A thorough comparison of the simulated and measured patterns of concentration changes was not possible because the observations did not show a uniform pattern. The general impression is that simulation results showed a much larger amplitude in the concentrations than the average of the measured data. This difference is not surprising because the pattern of the observed average concentrations is damped compared to the individual measurements. Moreover, concentration measurements during dry periods are missing which gives the impression that the concentration is fairly constant. The occurrence of peaks and dips in the simulated concentrations did not clearly deviate from the measured pattern, taking into account the uncertainty in the observed pattern.

Plot with pristine levels of N and S deposition

The performance of NuCSAM in simulating the measured concentrations on the plot with clean deposition was mostly similar to the results for the plot with ambient deposition (Table 7). Only the C-index for NO_3 was much higher, which is mainly due to the overestimation of the measured concentrations in the summer of 1993 (Fig. 4a, b and c). Comparison of the observations on the roofed plots with ambient and pristine deposition showed that deposition reduction led to a slightly significant decrease in SO_4, NO_3 and Al. Application of NuCSAM also showed that deposition reduction clearly led to lower simulated NO_3, SO_4 and Al concentrations at all depths. It is, however, not always directly clear from the figures whether the model overestimated or underestimated the decline in concentrations due to deviations between the simulated and measured concentrations. To make a comparison easier the average decline in the measured and simulated concentrations was calculated. This average decline was calculated from the difference between the two plots, for each point in time where both measurements and simulation results were available. The quotient of the change in simulated and measured concentrations can be used as a measure of the degree of underestimation (quotient <1) or overestimation (quotient >1) of the effect of deposition reduction by NuCSAM (Table 9).

NuCSAM overestimated the reduction in SO_4 concentrations at 90 cm depth. At 10 and 45 cm depth measured concentrations changes were well matched. The reason for the poor simulation of the SO_4 concentrations at 90 cm depth at the clean plot is not clear. Both this study and previous studies (Groenenberg *et al.*, 1995) did not give any indication that the process description used for SO_4 adsorption may lead to erroneous results. Accordingly, the observed deviation between the measured and simulated decline in SO_4 concentrations at 90 cm depth is probably due to poor parameterisation of the SO_4 adsorption parameters at the clean plot.

The average reduction in NO_3 (and Al) concentrations is overestimated at 10 and 90 cm depth and underestimated at 45 cm depth. The overestimation is mainly due to the strong reduction in the height of the summer NO_3

Table 9. The quotient of the change in simulated and measured concentrations upon a reduction in N and S deposition.

Element	Depth (cm)		
	10	45	90
SO_4	1.05	0.98	1.59
NO_3	1.47	0.63	1.03
Al	2.32	0.75	1.66

peaks, whereas the effect on the low winter concentrations appears to be underestimated by NUCSAM. Conclusions based on these results should be drawn cautiously because inherent differences exist between the two subplots due to spatial variability. These differences could not be taken into account because they are difficult to quantify due to the lack of an initial period in which both subplots are treated in the same way. On the basis of the results for the plot with ambient deposition, where NuCSAM underestimated N uptake upon a reduction in N deposition, a slight underestimation of the effect of the reduction in N deposition would have been expected. However, this expectation is not clearly confirmed by the above results. The deviation of Al is more difficult to explain because it is influenced by both the NO_3 and SO_4 inputs.

Conclusions

Attempts to validate the behaviour of NuCSAM, in predicting the effect of a reduction in S and N deposition, caused by the roofing of one of two forest plots were frustrated because of the large spatial varaibility within the individual plots. Despite these limitations, an evaluation of the model performance was carried out, taking into account the inherent uncertainties in the dataset. Nevertheless, the simulated ion concentrations at 45 and 90 cm depth were generally within the 95% confidence interval of the measurements. Concentrations in the topsoil of the ambient plot were slightly underestimated most probably due to deviations between the calculated and actual hydrological situation. Nitrate concentrations in the ambient plot were overestimated by the model, especially in 1990 and 1991, caused by an underestimation of the N uptake, an overestimation of the (net) mineralization during dry periods and probably an underestimation of the denitrification flux during wet periods.

The effect of the reduction in S deposition on the concentrations in the topsoil is well simulated by the model although at 90 cm depth the reduction in SO_4 concentrations was somewhat overestimated because of a poor parameterization of the SO_4 adsorption formula. The model overestimated the effect of a reduction in N deposition at 10 and 45 cm depth, whereas results were well simulated at 90 cm depth.

The major problems encountered in the model evaluation were: (i) the large spatial variability within each of the two subplots, which led to a large uncertainty in the validation of the models. (ii) the limited length of the measurement period and (iii) the lack of concentration measurements in the period directly after roofing and (iv) the lack of a full dataset providing hydrological, biological and geochemical data for the two subplots. Statistical analyses of the measurements showed no significant effect of deposition reduction due to the lack of concentration measurements directly after roofing. This negative effect of variability could have been reduced by a longer measurement period including an initial period with the same treatment on both plots. Due to the limited length of the data period and inherent differences between the plots it was difficult to judge the magnitude of the simulated effect of the deposition reduction by means of a comparison of observed and simulated concentrations. Apart from the problems directly arising from the spatial variability and the length of the monitoring period, this study would have provided more insight into the validity of the process formulation used in the model if a complete dataset of both subplots had been available.

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Appendix: Description of the most important processes included in NUCSAM

1. *Foliar uptake and foliar exudation*

$$FNH3_{fu} = frNH3_{fu} \cdot FNH3_{dd}$$

$$FX_{fe} = krX_{fe} \cdot A_{lv} \cdot ctX_{lv};\ X = \text{Ca, Mg, K}$$

2. *Litterfall and root decay*

$$FX_{lf} = krX_{lf} \cdot A_{lv} \cdot ctX_{lv};\ X = \text{M, S, Ca, Mg, K}$$

$$FX_{rd} = kr_{rd} \cdot A_{rt} \cdot ctX_{rt};\ X = \text{N, S, Ca, Mg, K}$$

3. *Mineralization*

$FX_{mi} = FX_{mi\ lt} + FX_{mi\ fm} + FX_{mi\ hu} + FX_{rd}$; X = N, S, Ca, Mg, K

$FX_{mi\ lt} = (kr_{mi\ lt} + kr_{tr\ lt}) \cdot A_{lt} \cdot ctX_{lt}$; X = N, S, Ca, Mg, K

$FX_{mi\ fm} = (kr_{mi\ fm} + kr_{tr\ fm}).\ ctX_{fm}$; X = N, S, Ca, Mg, K

$FX_{mi\ hu} = kr_{mi\ hu} \cdot A_{hu} \cdot ctX_{hu}$; X = N, S, Ca, Mg, K

$FX_{mi\ rn} = kr_{mi\ rn} \cdot A_{rn} \cdot ctX_{rn}$; X = N, S, Ca, Mg, K

Rate constants and fractions describing mineralization, are given as maximum values, which are reduced for a high ground water level. Mineralization rate constants for N are reduced at low N contents.

4. *Net Growth*

$$dAst = krgrl * Ast\left(1.0 - \frac{Ast}{Astmx}\right)$$

$$dAbr = frbrst * dAst$$

in which *dAst* and *dAbr* is the growth of stems and branches respecitively.

$$FX_{gu} = dAst \cdot ctXst + dAbr \cdot ctXbr$$

5. *Root uptake*

$FX_{ru} = FX_{gu} + FX_{lf} + FX_{fe} - FX_{fu} + FX_{rd}$; X = N, S, Ca, Mg, K

Distribution of N over NO_3^- and NH_4^+

$$FNH_{4\,ru} = fr_{pr}NH_{4\,ru} \cdot \frac{cNH_4}{cNH_4 + cNO_3} \cdot FNH_{ru}$$

$$FNO_{3\,ru} = FN_{ru} - FNH_{4\,ru}$$

6. *Nitrification and denitrification*

$$FNH_{4\,ni} = \theta \cdot D \cdot kr_{ni} \cdot cNH_4$$

$$FNO_{3\,de} = \theta \cdot D \cdot kr_{de} \cdot cNO_3$$

7. *Protonation*

$$FRCOO_{pr} = \theta \cdot D \cdot kr_{pr} \cdot cRCOO$$

In which CRCOO is the sum of dissociated and non-dissociated organic acids.

8. *Carbonate dissolution/precipitation*

$$FCa_{we\ cb} = \rho \cdot D \cdot krCa_{we\ cb} \cdot ctCa_{cb} \cdot (cCa_e - cCa)$$

$$cCa_e = KCa_{cb} \cdot \frac{pCO_2}{(cHCO_3)^2}$$

with: cCa_e equilibrium concentration
pCO_2 partial CO_2 pressure

9. *Weathering of primary minerals*

$FX_{we\ pm} = \rho \cdot D \cdot krx_{we\ pm} \cdot ctx_{pm} \cdot cH^{\alpha(x)}$; X = Ca, Mg, K, Na

$FAl_{we\ pm} = 3 \cdot FCa_{we\ pm} + 0.6 \cdot FMg_{we\ pm} + 3 \cdot FK_{we\ pm} + 3 \cdot FNa_{we\ pm}$

(based on the congruent weathering of equal amounts of Anorthite (Ca), Chlorite (Mg), Microcline (K) and Albite (Na))

10. *Aluminium hydroxide dissolution/precipitation*

$$FAl_{we\ ox} = \rho \cdot D \cdot krEl1 \cdot \exp(krEl2 \cdot ctAl_{ox}) \cdot (cAl_e - cAl)$$

$$cAl_e = KAl_{ox} \cdot cH^3$$

with: cAl_e = equilibrium concentration and *kr*Elo1 and *kr*Elo2 are Elovich constants

11. *Cation exchange*

$$\frac{frX_{ac}}{frCa_{ac}^{z_x}} = KX_{ex} \cdot \frac{cX^2}{cCa^{z_x}}$$

X = H, Al, Mg, K, Na, NH_4

z_x valence of cation X

12. *Sulphate adsorption*

$$ctSO_{4ad} = \frac{SSC \cdot KSO_{4ad} \cdot cSO_4}{1 + KSO_{4ad} \cdot cSO_4}$$

13. *Dissolution/speciation of inorganic C*

$$cHCO_3 = KCO_2 \cdot \frac{pCO_2}{cH}$$

Notation used for the model parameters

Entities	Compartments	Constituents	Processes			
A	amount (kg ha^{-1})	N	*dd*	dry deposition	*ac*	adsorption complex
c	concentration in the	NO_2	*de*	denitrification	*ad*	sorption site
	soil solution (mol_c m^{-3})	NO_3	*dw*	wet deposition	*cb*	carbonates
ct	content ($mmol_c$ kg^{-1})	NH_3	*ex*	exchange	*lv*	leaves/needles
CEC	cation exchange	NH_4	*fe*	foliar exudation	*ox*	oxides
	capacity ($mmol_c$ kg^{-1})	S	*fu*	foliar uptake	*pm*	primary minerals
D	layer thickness (m)	SO_2	*gu*	net (growth) uptake	*rt*	roots
fr	fraction (–)	SO_4	*le*	leaching	*st*	stems
fp	preference factor (–)	Ca	*lf*	litterfall	*lt*	litter
F	flux (mol_c ha^{-1} yr^{-1})	Mg	*mi*	mineralization	*hu*	humus material
kr	rate constant (yr^{-1})	K	*ni*	nitrification	*fm*	fermented material
K	equilibrium constant(mol^x l^y)	Na	*pr*	protonation		
ρ	bulk density (kg m^{-3})	Cl	*rd*	root decay		
SSC	sulphate sorption	H	*ru*	root uptake		
	capacity ($mmol_c$ kg^{-1})	Al	*we*	weathering		
θ	volumetric moisture	HCO_3	*td*	total deposition		
	content (m^3 m^{-3})	RCOO	*tr*	transformation		
		CO_2				